

ELECTRON SPIN RESONANCE OF ISOLATED COAL MACERALS: A PRELIMINARY SURVEY

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INTRODUCTION

While there have been a large number of electron spin resonance (ESR) studies of coal and coal products,⁽¹⁾ previous interpretations were based on the "average" properties of coals due to the chemical heterogeneity of the coal samples examined. The recent evolution of maceral separation techniques permits detailed ESR observations on coals of different rank, for which maceral type, and maceral density can be discriminated simultaneously. The present ESR survey of carbon radicals in separated macerals shows that each maceral type exhibits characteristic carbon radical properties. Furthermore, the properties of carbon radicals change within a given maceral type as the density varies.

EXPERIMENTAL PROCEDURES

A total of 37 samples from 16 coals of the Pennsylvania State University coal data base (PSOC) were examined. Separate fractions were obtained by isopycnic density gradient centrifugation of small ($\sim 3\mu$ m) coal particles in a aqueous CsCl density gradient.⁽²⁾ The individual samples are listed by PSOC numbers, maceral type, and density, in Table 1. After separation, the samples were kept under dry nitrogen until they were transferred to ESR tubes and sealed under helium gas. Typical ESR sample weights were approximately 10 mg. The ESR observations were conducted at 9.5 GHz in a Varian E-line ESR spectrometer with variable temperature capabilities from 90K-300K. The g-value, linewidth (defined as the splitting between peaks of the derivative curve of the ESR absorption - ΔH_{pp}) and the intensity of the carbon radical signal were observed in each case.

Before discussing the correlation of these properties, it is useful to note a significant difference in the response of carbon radicals in different maceral types to the applied microwave field. At sufficiently low microwave powers, the radical intensity varies linearly with microwave field strength, or equivalently varies as the square root of the microwave power. At higher powers, this response is less than linear, a phenomenon known as saturation, when the microwave power absorbed by the carbon radicals exceeds the radicals' ability to dissipate it to their environment. This process is illustrated in Figure 1, where the radical intensity, divided by the square root of the microwave power, is plotted as a function of the logarithm of the microwave power. The flat response at low power indicates the linear behavior; the fall-off at higher microwave

powers indicates the onset of saturation. It is clear from Figure 1 that vitrinite saturates at low powers, a fall-off being noted already at $\sim 10 \mu$ Watts of microwave power. A similar departure from linear behavior does not occur in inertinite until powers of $\sim 10^4 \mu$ W are applied. Exinite is intermediate in behavior. To avoid saturation-related problems, all samples were run at microwave powers of 3μ W, indicated by the arrow and dashed-line in the figure.

EXPERIMENTAL RESULTS

Examination of the ESR linewidth and the maceral density show clear distinctions between different maceral types. Figure 2 shows that exinite macerals have low densities and a narrow range of ESR linewidths, $\Delta H_{pp} \sim 6.5$ G. While vitrinite and inertinite show considerable overlap in maceral densities, the inertinite linewidths are dramatically smaller, $\sim 1-2$ G, as opposed to $\sim 5.5-7.5$ G for the vitrinites. This significant linewidth difference may assist in the discrimination of maceral types. As Figure 2 indicates, two macerals which petrographic analyses indicated to be inertinite, fall into the vitrinite maceral field. Since the small particle size required for separation ($\sim 3 \mu$ m) complicates the petrographic analysis, combined ESR and petrographic examinations may prove useful in future maceral type determinations. It is also interesting to note a weak trend in the vitrinite of decreasing ΔH_{pp} with increasing maceral density. Such a decrease might be anticipated if the increased maceral density resulted from a larger fraction of aromatic species, reducing proton broadening of the carbon radical linewidth.

The relationship between ESR intensity and maceral density is far less obvious, as Figure 3 indicates. Exinite samples have relatively low densities and radical intensities, as might be anticipated for aliphatic-rich macerals. Vitrinite and inertinites exhibit intensity variations in excess of an order-of-magnitude, and there is no clear variation of intensity with the physical density of the macerals. This suggests that a variety of factors, including the nature of the organic species and the details of the coalification process may serve as determinants of the number of carbon radicals.

A direct comparison of ESR linewidth and intensity, shown on Figure 4, shows a significant dependence on the type of coal sample being examined. In this case, open-circle symbols designate PSOC 106 samples, open-squares - PSOC 297, and open-triangles PSOC 1005. Solid-circles designate the balance of the vitrinite samples examined. No obvious clustering of vitrinite samples of a single type is observed. The fact that ΔH_{pp} is nearly independent of ESR intensity suggests that unresolved hyperfine interactions with adjacent protons, rather than dipole interactions between carbon radicals, are responsible for the observed linewidth.

The ESR linewidth variation with density for vitrinite macerals of different coals is presented in Figure 5. The open-symbols designate the three PSOC coals mentioned in Figure 4. As suggested in Figure 1, there is a general tendency for linewidth to decrease with increasing density. For PSOC 106 and 297, there is little density or linewidth variation observed for the vitrinites from each coal. Conversely, PSOC 1005 shows a broad range of density variations, and the linewidth increases. The source of this different behavior is still under investigation.

The isolated inertinite macerals provide an opportunity to examine their distinctly different properties. While strikingly narrower than the exinite and vitrinite ESR signals, the ESR absorption is still symmetric. The linewidth varies dramatically, from $H_{pp} = 0.89 - 2.00$ Gauss, and the linewidth is temperature independent. The intensity of the resonance absorption varies approximately as I/T , the Curie-like susceptibility expected for simple magnetic spins. Motion of these radical species could account for the relatively narrow linewidth.

CONCLUSION

We have successfully examined a suite of very small (~ 10 mg) samples by ESR. Different maceral types have strikingly different saturation behavior and are readily distinguished in a H_{pp} /density analysis. Radical intensities vary widely and are not related to physical density. Surveys of vitrinites from three of the PSOC coals suggest that intensities are reasonably similar within a given coal, but can vary significantly from one coal to the next.

At present, we are correlating these results with microanalysis of elemental composition and solid state ^{13}C NMR estimates of carbon aromaticities. These studies will be reported elsewhere.

ACKNOWLEDGMENT

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TABLE I: MACERAL RESUME
(Indicated numbers are the maceral densities in gm/cm³)

<u>PSOC #/Maceral Type</u>	<u>Vitrinite</u>	<u>Exinite</u>	<u>Inextinite</u>
1	1.257	-	-
81	WHOLE COAL	-	-
106	1.291	1.191	1.413
	1.330	-	1.447
	1.334	-	1.475
	1.371		
151	1.385		
236	1.278		
240	1.407		
268	1.272		
285	1.276		
297	1.264	1.040	1.384
	1.271	1.149	1.436
	1.305	1.165	
	1.340	1.200	
		1.207	
317	1.317		
409	1.302		
592	1.306		
594	1.332		
852	1.314		
975	1.408		
1005	1.345		
	1.382		
	1.420		
	1.455		
	1.486		

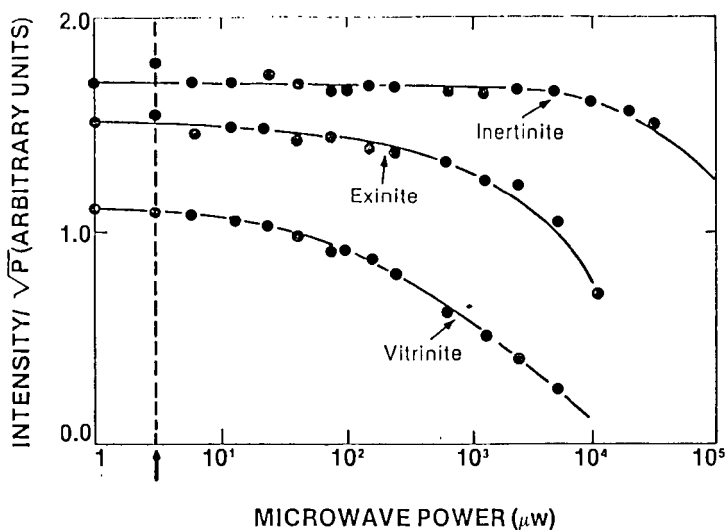


FIGURE 1: The various maceral types exhibit distinctly different microwave saturation properties.

FIGURE 2:

ESR linewidth, maceral density plots discriminate maceral types:

- ▲ = Exinite
- = Vitrinite
- = Inertinite

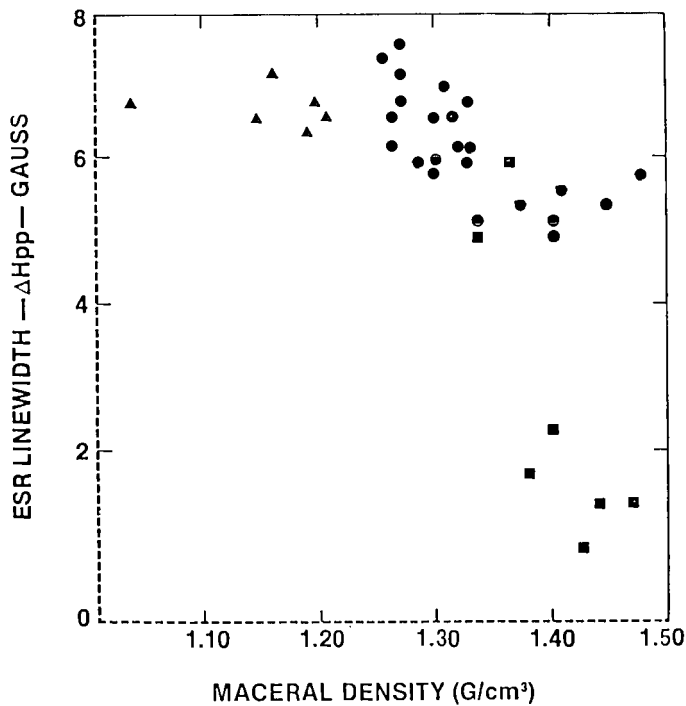


FIGURE 3: Carbon radical intensities do not depend explicitly on maceral type or maceral density.

- ▲ = Exinite
- = Vitrinite
- = Inertinite

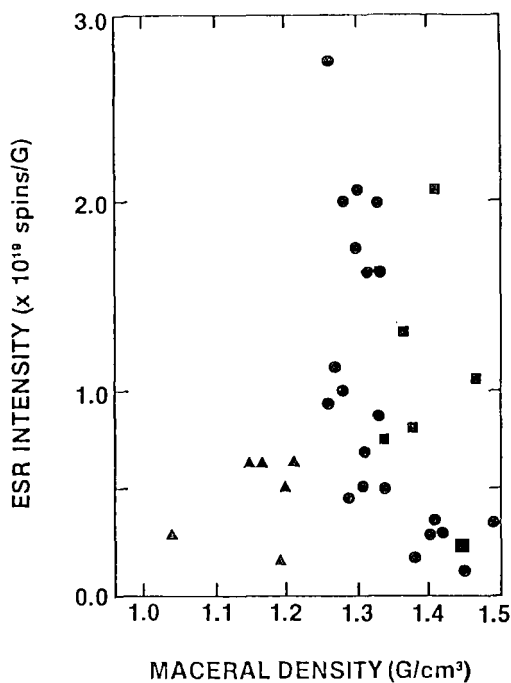
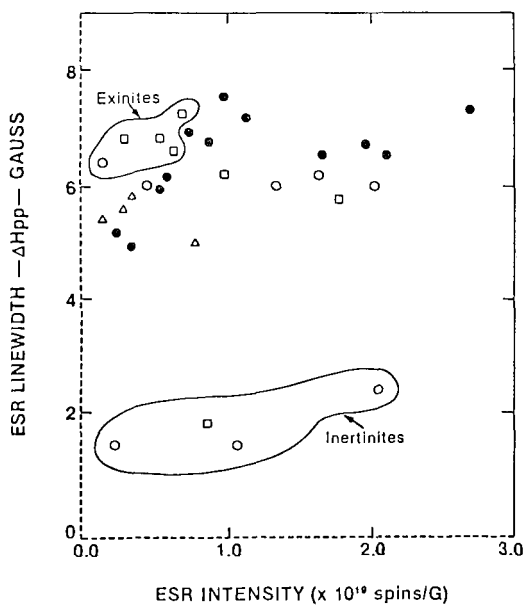


FIGURE 4: A weak variation of ESR linewidth on ESR radical intensity is observed.

- = PSOC 106
- = PSOC 297
- △ = PSOC 1005
- = All other Vitrinites



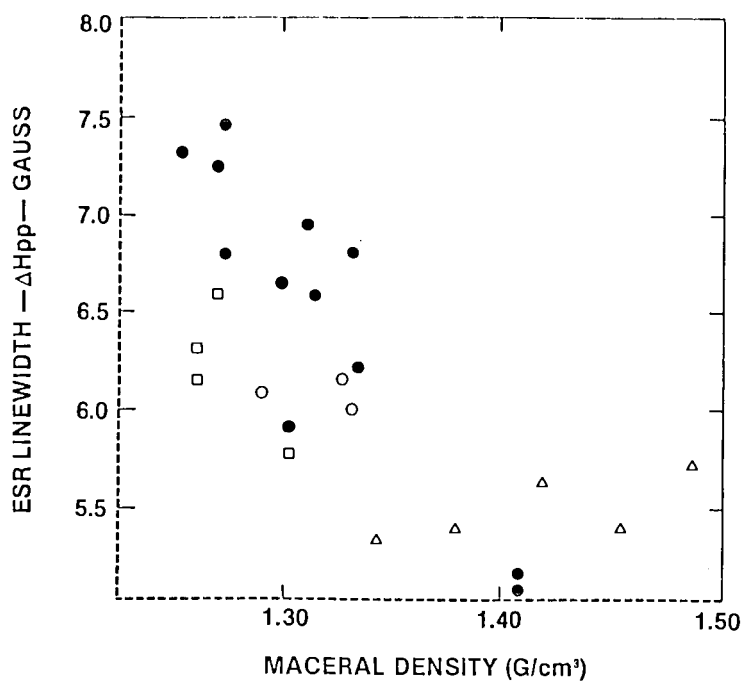


FIGURE 5: A weak decrease in ESR linewidth with maceral density is observed for vitrinite macerals. Little systematic change is observed for macerals from a given coal.

○ = PSOC 106

□ = PSOC 297

△ = PSOC 1005

● = All Other Vitrinites